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Hydrogen and Gaseous Fuel Safety and Toxicity

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Non-traditional motor fuels are receiving increased attention and use. This paper examines the safety of three alternative gaseous fuels plus gasoline and the advantages and disadvantages of each. The gaseous fuels are hydrogen, methane (natural gas), and propane. Qualitatively, the overall risks of the four fuels should be close. Gasoline is the most toxic. For small leaks, hydrogen has the highest ignition probability and the gaseous fuels have the highest risk of a burning jet or cloud.

I. INTRODUCTION

With the increased use of non-traditional motor vehicle fuels in place of gasoline, the issue of safety with these fuels must be addressed. Each potential replacement for gasoline holds some safety advantages and disadvantages. This paper gives a comparison of several of the leading gaseous fuels, herein called gases, and gasoline. The gaseous fuels of interest are hydrogen, propane (liquefied petroleum gas [LPG]), and methane (natural gas). Hydrogen may be cryogenic liquid (LH2) or compressed (CH2). Natural gas may be compressed (CNG) or liquid (LNG). There have been several published studies performing general comparisons, and these will be drawn upon in this work. This discussion focuses on the physical and chemical hazards associated with fuel handling for the four subject fuels. Table I gives some general data on the fuels under consideration.

II. PHYSICAL HAZARDS

There are several physical hazards inherent with each type of motor fuel. The physical hazards with fuels are addressed here as energy forms: acoustic, electrical, thermal, and pressure energies. Other energies, such as gravitational, kinetic, mechanical, and vibration energies are not treated in detail because, according to the operating experiences, these energies are not major safety concerns for handling motor fuels. Each of the identified energy forms is discussed below.

II.A. Acoustic Energy

The acoustic energy generated by gas flowing through lines can create acoustic frequencies, typically several hundred hertz, and subsequently cause fatigue failure of the components involved. Melese and Katz discuss the design for acoustics in gas flow.[1] However, acoustic vibration is usually a concern only for large gas flows of many kg/s to Mg/s; vehicle fueling will be much less than that level of flow.

This difference in flow rates does not imply that acoustics can be ignored in design. Acoustics must be considered in the analysis of gas piping systems, but other hazards are more prevalent for common users. The analogous situation with liquids, such as gasoline, is pressure pulsations (referred to as "water hammer"). Like the fuel gases, the liquid pressure and flow rate are low in refueling. Therefore, water hammer or pressure pulsation is only an issue with large flow applications: bulk deliveries, pipelines, or other large-scale operations.

II.B Electrical Energy

Electrical energy as discussed here dwells on electrostatic charge. Three scenarios should be considered: when vehicles travel, when they are refueled, and when persons refueling have an electrostatic charge. When motor vehicles travel they can acquire an electrostatic charge. This charge dissipates quickly (seconds or less) through the resistance of tires and concrete surfaces (asphalt surfaces are more resistive than concrete). When fuel is dispensed into an automobile, if the refueling nozzle is in metal-to-metal contact with the fill opening (that is, electrically bonded to the car) then no special provisions are needed for the electrostatic charge generated by flowing hydrocarbon fuel. The third issue is electrostatic charge on persons performing refueling. The safety issue is that electrostatic discharges in the fractional milliJoule (mJ) energy range are adequate to ignite gasoline vapor and fuel gases.[2] In his case history of process plant disasters, Kletz discusses an event where a man drove to a gasoline station to refuel.[3] The attendant

Table I. Properties of Hydrogen, Methane, Propane, and Gasoline

Property[a]	Hydrogen	Methane	Propane	Gasoline
Molecular Weight, amu	2.016	16.043	44.097	107
Triple point pressure, atm	0.0695	0.1159	1E-09	—
Triple point temperature, K	13.803	90.68	85.48	180 to 220
Normal boiling point (NBP) temperature, K	20.268	111.632	231.11	310 to 478
Critical pressure, atm	12.759	45.387	41.937	24.5 to 27
Critical temperature, K	32.976	190.56	369.82	540 to 569
Density at critical point, g/cm^3	0.0314	0.1604	0.2163	0.23
Density of liquid at triple point, g/cm^3	0.077	0.4516		—
Density of solid at triple point, g/cm^3	0.06865	0.4872		—
Density of vapor at triple point, g/m^3	125.597	251.53		—
Density of liquid at NBP, g/cm^3	0.0708	0.4226	0.582	0.7
Density of vapor at NBP, g/cm^3	0.00134	0.00182	0.00242	0.0045
Density of gas at NTP, g/m^3	83.764	651.19	1858	4400
Density ratio: NBP liquid to NTP gas	845	649	313	156
Heat of fusion, J/g	58.23	58.47	94.98	161
Heat of vaporization, J/g	445.59	509.88	425.31	309
Heat of sublimation, J/g	507.39	602.44		—
Heat of combustion (low), kJ/g	119.93	50.02	46.45	44.5
Heat of combustion (high), kJ/g	141.86	55.53	50.48	48
Energy density, MJ/liter	8.49	21.14	22.8	31.15
Specific heat (Cp) of NTP gas, J/g-K	14.89	2.22	1.625	1.62
Specific heat (Cp) of NBP liquid, J/g-K	9.69	3.5	2.213	2.2
Specific heat ratio (Cp/Cv) of NTP gas	1.383	1.308	1.131	1.05
Specific heat ratio (Cp/Cv) of NBP liquid	1.688	1.676		—
Viscosity of NTP gas, g/cm-s	0.0000875	0.00011	0.000079	0.000052
Viscosity of NBP liquid, g/cm-s	0.000133	0.00113	0.0019	0.002
Thermal conductivity of NTP gas, mW/cm-K	1.897	0.33	0.152	0.112
Thermal conductivity of NBP liquid, mW/cm-K	1	1.86	1.34	1.31
Surface tension, N/m	0.00193	0.01294	0.00702	0.0122
Dielectric constant of NTP gas	1.00026	1.00079	1.0020	1.0035
Dielectric constant of NBP liquid	1.233	1.6227		1.93
Index of refraction of NTP gas	1.00012	1.0004		1.0017
Index of refraction of NBP liquid	1.11	1.2739		1.39
Adiabatic sound velocity in NTP gas, m/s	1294	448	249	154
Adiabatic sound velocity in NBP liquid, m/s	1093	1331		1155
Compressibility factor (Z) of NTP gas	1.0006	1.0243	1.0193	1.0069
Compressibility factor (Z) in NBP liquid	0.01712	0.004145		0.00643
Gas constant (R), cm^3-atm/g-K	40.7037	5.11477	1.86083	0.77
Isothermal bulk modulus of NBP liquid, MN/m^2	50.13	456.16		763
Volume expansivity (b) of NBP liquid, /K	0.01658	0.00346		0.0012
Percentage of thermal energy radiated from diffusion flame to surroundings, %	17–25	23–32	27-30	30–42

a. NTP = 1 atm and 20°C (293.15 K) normal temperature and pressure
NBP = normal boiling point.

handed the man the car's gas cap to hold while the attendant fueled the car. While holding the gas cap, the man removed his pullover sweater. The man was wearing non-conducting footwear (i.e., rubber-soled shoes), so the electrostatic charge generated by removing the sweater did not dissipate to the ground. When the man began to replace the gas cap, the static charge created a spark that jumped from the gas cap to the car's gas fill port. The spark provided sufficient energy to ignite the gasoline vapors in the air near the port and a fire started at the refueling nozzle. The fire was quickly extinguished. Note that this fire could not have propagated into the fill nozzle because the gasoline vapor mixture is much too rich in the fill port. Electrostatic charge buildup is an important factor in motor fuel safety for both gasoline vapors and gaseous fuels. Proper grounding and bonding is necessary to prevent fuel combustion during handling operations. In general, existing codes and standards address proper bonding: the fill nozzle must contact the fill port.

II.C. Thermal Energy

Thermal energy refers to the thermodynamic state of the fuels under scrutiny. Hydrogen may be used at cryogenic temperature (20 K) or at ambient temperature, depending on the means used to store fuel on the vehicle. Methane may also be used at cryogenic temperature (111 K) or at ambient temperature, and propane is usually pressure-liquefied gas at several atmospheres pressure and ambient temperature (300 K). Gasoline is typically used at ambient temperature as well.

The inherent thermal energy of cryogenic liquids or cold gases poses hazards to people. Contact or immersion on bare skin can freeze body parts.[4] A typical person's skin temperature is 35°C (95°F). Cooling skin by exposing it to liquid, cold gas, or cold metal parts that reduce the skin's temperature to below −3°C (27°F) causes the formation of ice crystals in the body's skin cells.[5] Even escaping propane gas jets can be very cold and have cooled skin sufficiently to produce burns.[6,7] Propane fill hose leaks have cooled enough to freeze a consumer's hand to the fill nozzle, which is typically a concern with LNG or LH2. Of all these fuels, gasoline is the most benign at ambient temperature.

II.D. Pressure Energy

Pressure energy discussed here refers to the storage pressure of the fuel onboard the vehicle or at the refueling station. Hydrogen might be stored at low pressure as a cryogenic liquid (i.e., ≈ 0.3 MPa) or at very high pressure as a compressed gas (up to ≈ 60 MPa). Methane is expected to have similar properties, ≈ 0.2 MPa as a cryogenic liquid or up to ≈ 40 MPa as a compressed gas. Propane at 300 K liquefies at ≈ 4 MPa, so the operating pressure would be slightly above that threshold. Gasoline is stored a very low pressure of $\approx$0.1 MPa. For this form of energy, gasoline is the most benign of the fuels considered.

Note that cryogenic pressures are not a threat unless confinement is lost. Without confinement, large liquid-to-gas expansions can occur, which can generate reasonably high pressures in the cold gases. High-pressure gases present several hazards. Exposure to a high-pressure gas jet at close range, such as if a fault occurred during refueling line handling, can lead to skin incision and skin injection injuries. Brauer states that such injuries can occur at 4.4 MPa and higher.[8] The eyes are a particular concern because of their fragility under high-pressure exposure. All of the gaseous fuels pose a hazard in this regard. As a generality, physicians express greatest concern when a non-toxic gas injects foreign materials into the skin (e.g., metal shavings, dust, oil, or rust particles from the gas system). Otherwise, non-toxic gases will tend to evolve back out of the skin, but at a much slower rate than that at which the gas entered (i.e., days or weeks versus seconds).

Another pressure concern is hose whip. If the refueling hose were to become disconnected or fail while under pressure, the escaping gas would propel the hose at high velocity with random, unpredictable motion. In the nuclear industry, a pipe whip analysis has traditionally been performed for a breached, steel-walled pipe when the system pressure was over 1.9 MPa, so flexible hose whip would be a concern at lower pressures.[9] Workers in other industries (e.g., spray painting, sand blasting, and compressed air supply for pneumatic tools) often use tethers, called "whip checks," on hoses to reduce the threat of being struck by a whipping hose. Impulse impacts from a flailing hose could be physiologically damaging for the MPa gas pressures under consideration. Thus, there are engineered safety features of positive connection fittings on the gas lines and quick shutoff valves to limit gas flow.

A further consideration is the stored pressure energy in the station and vehicle tanks. If any part of the pressure boundary fails, such as a fitting or instrument, it could be propelled outward at high velocity because of the high pressures. Using formulas from Baum for an arbitrarily selected 50-gram piece propelled from the hydrogen, methane, or propane pressurized gas systems gives values of well over 79 J for hydrogen and methane, and ≈ 10 J for propane.[10] A fragment is generally considered to produce a critical injury or lethal hazard if its kinetic energy is 79 J or greater, although fragments with 40 to 60 J can also cause serious wounds.[11] With a person standing between the pump unit and vehicle tank, the likelihood of being struck by a failed part expelled under pressure is reasonably high. Therefore, pressure part failures are important for high-pressure gas storage of gaseous motor fuels. The stored energy in pressurized gas systems must be respected; even 13 MPa gas cylinders weighing 62 kg have sufficient thrust to launch themselves upward at velocities of tens of m/s when the gas valve has been sheared from the cylinder body.[12] Table II gives a comparison of the results from these potential hazards. In general, engineering controls have been designed and installed on traditional and alternate fuel vehicle refueling stations, particularly natural gas refueling stations, to manage the hazards.[13–20]

A final pressure consideration is the occupational injury rates from gasoline stations. The Bureau of Labor Statistics data shows a total recordable injury case rate of 3.6, 3.4, and 3.4 cases per 100 full-time workers for the years 2003 through 2005 for code 447 (gasoline stations), respectively.[21] These values are roughly 25% below the U.S. national average for total recordable injury rates. Therefore, the gasoline station employees are either protected by engineering control measures or the work they are employed to perform is of a non-hazardous nature (i.e., cashier or clerk rather than hands-on work as attendants). Presently, the number of alternate fuel stations in the U.S. is only about 5,000; there is no individual labor code for workers at these stations.

III. CHEMICAL HAZARDS

There are two areas of chemical safety concern when considering refueling with motor vehicle fuels. The first is the chemical toxicity of the fuel, and the second is combustibility. Both of these issues are important to workers in all parts of the chemical processs industry as well as consumers.

III. A. Toxicity

As an indication of toxicity, the suggested temporary emergency exposure limits (TEELs) for public exposures from the U.S. Department of Energy (DOE) are given in Table III.[22] TEEL-0 is a low concentration to which almost any person could be exposed without harm on an indefinite time basis. The American Conference of Governmental Industrial Hygienists (ACGIH) gives allowable threshold limit values (TLVs) for workers; these are given in Table III for comparison.[23] The ACGIH values are widely accepted in the U.S. and abroad. The National Fire Protection Association (NFPA) health hazard values in the table came from *Fire Protection Guide to Hazardous Materials*.[24]

Chemical toxicity has been a continual issue with gasoline. The ACGIH has identified gasoline as a confirmed animal carcinogen with unknown relevance to humans,[23] and the International Agency for Research on Cancer (IARC) has cited gasoline as possibly carcinogenic to humans.[25] The IARC points out that gasoline is a complex mixture of hydrocarbons, including 2–3% benzene, and benzene is positively carcinogenic to humans. There have been a number of research studies of station personnel and customer exposures to gasoline during refueling station operations.[26–32] As shown in the studies, public exposure to gasoline during refueling is typically small for two reasons: the exposure time is generally brief in any given month (gasoline flows at ≈ 10 gpm at refueling stations so typical automobiles only require a few minutes per refueling session and people do not always stand near the self-service refueling nozzle), and some states require vapor recovery systems to capture vapors emanating from the vehicle tank fill port. Hakkola and Saarinen give data considered to be representative of consumer exposures.[26] They show that average customer exposures to gasoline hydrocarbons are 29 ppm with a high value of 180 ppm in refueling sessions where the gasoline vapors were not collected, and an average of 6 ppm with a high value of 44 ppm for refueling with gasoline vapor recovery systems. The vapor recovery system showed a significant exposure decrease of a factor of ≈ 4. Comparing these exposures to the limits in Table III shows there is little cause for concern with these levels, even for the non-vapor recovery systems. Another potential concern besides vapor inhalation is skin contact or dermal exposure. Dermal exposure to gasoline has proven to be a skin irritant, but not a significant chemical irritant. Only long duration dermal exposures of several hours have produced severe skin irritation.[33]

Table II. Potential for Fuel-related Injury from Several Energy Sources

Fuel	Acoustic Energy	Electrostatic Energy	Thermal Energy	Pressure Energy
CH2	Low concern	High concern, must prevent	Low concern	High concern
LH2	Low concern	High concern, must prevent	High concern	Moderate concern
CNG	Low concern	High concern, must prevent	Low concern	High concern
LNG	Low concern	High concern, must prevent	High concern	Moderate concern
Propane	Low concern	High concern, must prevent	Low concern	High concern
Gasoline	Low concern	High concern, must prevent	Low concern	Low concern

Table III. Allowable Exposures to Respirable Vapors and Gases

Fuel	TEEL-0 (ppm)	ACGIH TLV (ppm)	Comments
Gasoline	300	300	NFPA health hazard = 1 (irritant, breathing protection may be needed, slight health hazard)
Hydrogen	4,000	Simple asphyxiant gas	NFPA health hazard = 0 (ordinary combustible material) In a static atmosphere room, H_2 would have to reach >60,000 ppm to displace O_2 to reach the 19.5% O_2 level defined as an oxygen deficient atmosphere. H_2 lower flammable limit is 4% in air, or 40,000 ppm, so that is a greater safety concern. From the TEEL explanations, TEEL-0 is 10% LEL or 4,000 ppm for H_2.
Methane	1,000	1,000	NFPA health hazard = 2 (intense or continued exposure could cause injury or incapacitation)
Propane	1,000	1,000	NFPA health hazard = 2 (intense or continued exposure could cause injury or incapacitation)

Gasoline leakage into ground water has also been a large concern across the U.S.[34] Gasoline entry into the ground water can lead to ingestion of hydrocarbons, benzene, etc. via drinking water. Leaking underground storage tanks have been a continual source of concern for gasoline service stations. In a 2004 publication, the U.S. Environmental Protection Agency (EPA) reported that over 1.5 million substandard tanks had been closed and 300,000 petroleum leaks had been cleaned up.[35]

The gaseous fuels do not have the same level of toxicity concern as gasoline and also have higher ppp exposure levels than gasoline. None are suspected carcinogens. Hydrogen is a simple asphyxiant gas with an NFPA health hazard rating of zero and no ACGIH threshold limit value. If hydrogen is stored as a cryogen or under pressure, then dermal contact is an important concern, but there is no chemical toxicity. Methane and propane have generalized inhalation exposure limits, as cited in Table III, based solely on their aliphatic hydrocarbon molecular structure. A report about two LPG accidents has suggested that persons exposed to gradually increasing levels of LPG in air may suffer from a central nervous system suppression effect, or LPG poisoning, that begins with nausea and headache while the blood concentration of propane increases with increasing concentration and prolonged exposure.[36] However, this is exposure to high concentrations of LPG, up to a few % of atmosphere, that caused persons in unventilated trenches to collapse; these symptoms are also associated with oxygen deprivation. Propane is generally considered to not be a toxicological threat, just an air displacement threat, and methane is typically considered to be biologically inert.[37,38] Like hydrogen, these gases can displace air but are not regarded to be chemically toxic.

Table IV. Combustion Properties of Hydrogen, Methane, Propane, and Gasoline

Property	Hydrogen	Methane	Propane	Gasoline
Quenching gap in NTP air, mm	0.64	2.03	1.78	2.0
Limits of flammability in air, volume %	4–75	5–15	2.1–9.5	1.4–7.6
Limits of detonation in air, volume %	18.3–59	6.3–13.5	3.4–7	1.5–3.3
Minimum spark energy in air for deflagration ignition, mJ	0.02	0.29	0.305	0.24
Autoignition temperature, K	858	813	740	501–744
Flame temperature in air, K	2,318	2,148	2,243	2,470
Maximum burning velocity in NTP air, cm/s	278	37–45	43–52	37–43
Energy release from stoichiometric mixture, MJ/m^3	3.58 (30% H_2)	3.58 (9.5% CH_4)	3.79 (4.0% C_3H_8)	3.91 (2% vapor)
NFPA flammability rating	4	4	4	3
NFPA instability rating	0	0	0	0
Data sources: Refs. 24 and 39.				

III.B Combustion

Combustion can occur in many forms. Table IV gives some combustion properties of the four fuels under consideration. For combustible gases, there is either a pre-mixed flame or a diffusion flame. A pre-mixed flame burns with the gas disbursed into the air and can burn in a flash fire/fireball, deflagration, or detonation. In a diffusion flame, air is drawn to the base of a stationary flame and diffuses into the combustion flame front. A flame jet is a diffusion flame.[40] A deflagration of gas dispersed in air is a rapid combustion event, where the combustion wave front moves at subsonic (≈ m/s, but still rapid) speed through the gas-air mixture. Deflagrations are explosions because there is overpressure, heat release, and generation of debris missiles.

Deflagrations have wide gas concentration limits in air, as seen in Table IV, and ignitions at the lean and rich limits tend to produce low energy and low pressure outputs. Deflagrations can be ignited by very modest energies.[41] However, Baker and Tang note that if the ignition source is weak (< Joules) the flame front will not accelerate sufficiently to create a shock wave that will damage the surroundings.[42] That is, a weak mJ ignition source would most likely lead to a flash fire/fireball deflagration with minimal overpressure rather than a strong deflagration with air blast overpressure effects.

Deflagrations of pre-mixed gas in air are often called unconfined vapor cloud explosions (UVCEs).[40,41] UVCEs tend to be inefficient, low yield combustion events, many being 1 to 2% of the heat of combustion of the total fuel available. Gugan does have data on a few events that reached up to 65% yield, but most of the recorded events were much less than 5%.[43] Many UVCEs occurred with very large releases, 30 or more tons of material released from a process plant or set of rail tank cars. A refueling station would typically be on the low end of UCVE release masses. Typical threshold quantities of gaseous fuels for chemical safety analysis are on the order of 5 tons, per 40 CFR 68; gasoline is not listed.[44] Gugan notes that UVCE analyses used a 2% yield when establishing separation distances for chemical process facility site planning.[43] However, 40 CFR 68.25 directs that 10% yield of available energy be used in a vapor cloud explosion calculation when assessing the explosion damage zone.[44] Deflagrations can be serious events, presenting radiant heat release and overpressure to on- and off-site personnel and plant equipment.

Detonations are the most severe explosions, generating the highest overpressures, heat energy releases, and kinetic energy debris missiles. Detonations require higher concentrations of gas in air, typically some turbulence or reflection to speed up the combustion wave front, and a strong ignition source (Joules to kilo Joules) to initiate a rapid combustion wave front.[45] It is also possible to "run up" or experience a deflagration-to-detonation transition in events with appropriate precursors. These precursors are a high mass (tons) of gas mixed in air, reflection or turbulence on the deflagration wave front to speed it up, and a reasonably strong ignition source to create an initially high m/s velocity combustion wave front.

Hydrogen combustion differs from other combusting hydrocarbons. As Ringland[46] points out, hydrogen has the widest flammable range, but flammable limit ranges in open air environments tend to not be as important as the lower limit value because dispersion and diffusion in air act to limit gas concentrations to small values. Hydrogen is much lighter than air and tends to rise no matter what the gas temperature or room air temperature. In general, considering refueling operations under an awning or pavilion, small hydrogen leaks that are naturally buoyant should disperse to air quite readily. Swain and Shriber studied gaseous fuel and gasoline releases in a residential garage and the hydrogen easily dissipated, leaving only a small flammable region (even with a large leak of 1,000 L/hr).[47] The same was true for methane, but propane and gasoline vapors lingered in the garage. Unless there is a static discharge ignition or some other ignition source at or near the hydrogen release point (e.g., an operating automobile engine, overheated engine parts, or a flame), hydrogen gas could be expected to dissipate to the ambient environment. Larger leaks pose more of a concern to persons nearby and more of a combustion hazard. Escaping hydrogen gas can generate its own static charge; a static discharge to ground from the edge of the gas jet is small but sufficient energy to ignite the hydrogen.[48] This phenomenon has been seen in several situations with gaseous hydrogen and cryogen boiloff hydrogen release.[5]

Hydrogen flames are typically non-luminous to the naked eye unless some carbon-based fuel is also combusting with the hydrogen (e.g., paint, rubber hose, or electrical insulation). To avoid walking into a hydrogen flame, a fire protection good practice at suspected fire locations is to hold out a broom and toss dirt ahead of the broom to probe the area. When the broom bristles and any combustibles in the dirt reach the edge of the hydrogen fire they will incandesce, immediately depicting the edge of the fire.[48] Of course, isolating any break locations is prudent from a safety as well as economic perspective.

There have been a few hydrogen powered vehicles, but the operating experience data are insufficient to draw any conclusions about hydrogen vehicle reliability or safety. Some initial estimates of hydrogen and other fuel ignition probabilities given a spill from road tankers (generally carrying up to 8,000-gal inventories) are given in Table V.[45] These values tend to be large because they are only estimates. Operating experiences will provide data to refine these estimates.

Table V. Conditional Probabilities of Gas or Vapor Ignition Given a Spill

Fuel	Small Spill	Large Spill
Immediate ignition upon spill initiation		
Gasoline	0.15	0.5
Hydrogen	0.5	0.9
Methane	0.25	0.9
Propane	0.25	0.75
Delayed ignition after spill initiation		
Gasoline	0.04	0.05
Hydrogen	0.45	0.09
Methane	0.50	0.09
Propane	0.68	0.23
Note: small spills are ≤ 10% of tank inventory; large spills are 100% of tank inventory, based on 8,000-gal inventories.		

An important aspect of all three gaseous fuels is that they are naturally odorless. The Code of Federal Regulations states that a combustible gas in a distribution line must contain a natural odorant so a concentration in air of one-fifth of the lower flammable limit is readily detectable by a person with a normal sense of smell.[49] Rivkin stated that depending on the technology used with hydrogen fuel, the hydrogen may not be odorized for safety.[20] The odorant, such as ethyl mercaptan, could foul the membranes in fuel cells. Odorant cannot be used with cryogenic liquids because the widely used odorizing compounds will freeze out of the liquefied gas. Gasoline does not require an odorant; it carries an inherent solvent smell that is easily detected by persons with a typical sense of smell. Odorants are certainly a useful, but not infallible, safety measure. Not all persons have a normal sense of smell.[50,51] Another odorant issue is that an odorized gas leaking from an underground pipe can be cleansed of odorant by the soil the gas passes through.

Like hydrogen, methane is lighter than air. Methane tends to burn with a blue-yellow flame that is easily recognized. As seen in Table IV, methane requires a spark of over a quarter-milliJoule for ignition in air.

Chamberlain and Modarres present a quantitative risk assessment of CNG buses.[52] The conclusions were that CNG-fueled buses were more susceptible to fires than diesel-fueled buses by a factor of about two. Note that one reason diesel fuel was adopted is because diesel fuel does not evolve flammable vapors until it is heated and is therefore safer than gasoline. Thus, the CNG results are not surprising because any CNG leak is always flammable. The risk frequencies for bus fires found by Chamberlain and Modarres are shown in Table VI.

Table VI. Risk Frequencies for Bus Fires with Given Cause

Cause	Risk Frequency (per bus-yr)
Electrostatic discharge of CNG	1.4E−05
Operator error	4E−02
Catastrophic failure of bus or station hardware	1.4E−03
Accident impacts mainly due to collision	3.6E−02

Melchers and Feutrill give occurrence probabilities for LPG ignition given an LPG leak at a refueling station.[53] The authors assumed 0.9 for immediate ignition (within 10 s, no mixing in air), 0.75 for early ignition, 0.5 for delayed ignition, and 0.33 for late ignition. Melchers and Feutrill recognized that these values are subject to considerable uncertainty, so they used very conservative estimates and attempted to incorporate data from the petroleum industry to support assumptions. The immediate ignition of 0.9 does not compare well with the 0.25 value from Table V, but the delayed ignition value of 0.5 compares reasonably well to the 0.68 value from the table. These data arise from speculative sources because the chemical process industry tends to be less highly regulated than the nuclear power industry. Even gasoline service station fires are not always centrally reported; only state fire marshals tend to be aware of fires at public stations in their own state. Fortunately, despite non-centralized reporting and difficulty with statistical data, both methane and propane are odorized for safety, to help alert people to leaks.

Gasoline has inherent fire hazards. In typical gasoline fires, the liquid gasoline burns in a flowing or stationary pool (dikes, bund walls) and vapor burns above the liquid surface. Obviously, confined pools are more readily dealt with than a burning, flowing liquid. The flashpoint of a liquid is defined as the lowest temperature at which a liquid will evolve enough vapor to ignite. Because gasoline is a low-temperature flashpoint material (−43°C [−45°F]), use of water for extinguishment is not optimum; water at 10 or 15°C (50 or 59°F) will not cool the gasoline sufficiently to preclude vapor production. Gasoline fires are usually extinguished by reducing contact with air. The gasoline pool surface is often covered with low-expansion foam;[48] water mist or fog can also be used but care must be taken not to spread the gasoline because gasoline floats on water. Gasoline should not be washed or swept into sewers because it would evolve vapor into a confined location that might allow a strong deflagration or a detonation. When gasoline burns, the flame is a bright orange and the smoke is dark, so the fire is easily noticed.

Gasoline vapors are heavier than air and tend to stay in low areas or flow along the ground. The vapors diffuse or mix slowly in air unless driven to mix by air currents; only large gasoline spills have resulted in deflagration explosions. Gasoline also rarely has a vapor cloud explosion. Gasoline has suffered from boiling liquid expanding vapor explosions (BLEVEs), where a gasoline tank is externally heated, such as by a pool fire. The gasoline in the tank boils and the tank either vents (adding its vented vapor to the fire but preserving the tank structure) or overpressurizes and ruptures (adding its shrapnel and gasoline inventory to the fire).[54] Fortunately, BLEVEs are rare events and are usually associated with refineries rather than dispensers (although an LPG BLEVE has occurred in a refueling station).[55] While retail gasoline service stations are routinely accepted by the public and are considered to be benign, some station fires occur every year. NFPA data give a quote of 1,530 vehicle fires initiated with vehicle fuel at U.S. public service stations in the 5 years between 1994 and 1998.[56] Using the Statistical Abstract of the U.S., there were 126,889 retail service stations in the U.S. in 1997.[57] Assuming this count remains reasonably constant over the 1994–1998 time period, the fire frequency is 1,530/[(5 years)(126,889)] or 2.4E−03 fires/station-year. McCarthy et al. also presented some information on gasoline station fires.[58] For California gasoline stations with vapor recovery from the refueling port, gasoline fires at stations were 8.41 fires per billion gallons sold over 1982–1984. For the fourteen states without gasoline vapor recovery at the refueling port, the fire rate was 17.02 fires per billion gallons sold. To convert these reported values for comparison with the calculated value above, an assumption of a modest, national average sales volume station was used (90,000 gallons/month or ≈ 1E+06 gallons/year). Conversion gave 8.4E−03 fires per station-year for stations with no vapor recovery and 1.7E−02 fires per station-year for stations with recovery. The 1980s and 1990s data are in reasonably good agreement; a fire frequency on the order of magnitude of 1E−03/year appears to be correct. This point estimate would be classified as an unlikely event in the DOE safety framework.[59]

Nabours discusses the fact that personal static electricity has caused some increase in station fires during recent years.[60] The Petroleum Equipment Institute, American Petroleum Institute, and the National Institute for Occupational Safety and Health (NIOSH) have all issued warnings about static electricity during refueling.[61–63] Pratt describes the static accumulation process during refueling of people re-entering a car and sliding on the car seat, building up a charge of at most several microCoulombs.[64] Greason also calculated similar values.[65] Then the person gets out of the car to remove the fill nozzle. If a person has conductive footwear, there is no ignition concern—any static charge accumulation will dissipate within one or two walking steps. If the person touches some metal of the car body while exiting the car they will also be discharged before coming near the gasoline fill port. If the person does not discharge, then a spark up to 20 mJ energy or more could occur when the person takes hold of the dispenser nozzle. Considering that gasoline has a small lower flammable limit and the region around the fill port is vapor rich because entering liquid forces tank vapors out to the air, it is not surprising that a flash fire could occur.

Another event of concern is the automobile drive-away event, which is when a vehicle leaves a gasoline pump with the nozzle still attached to the vehicle's fill port.[66] In the past, such events could lead to gasoline spilling onto the concrete surrounding the pump island. There is an engineering control that has been built into hose lines, however, called a break-away connector.[67] The breakaway connector shuts a butterfly valve when pulled apart so that gasoline spills are limited. These connectors can be resealed if the nozzle end of the hose is retrieved. Polling two self-service gasoline stations (a five-pump island station of 150,000 gallons/month and a four-pump island station with ≈ 55,000 gallons/month) in Idaho Falls, Idaho, for events over the past 6 and 8 years, respectively, revealed a tentative point estimate frequency for drive-away events of 0.5/station-year for these two stations. There is no reason to expect different results in other regions using self-service stations, but a larger sampling would give a higher statistical confidence in the frequency value. This 0.5/station-year frequency is large enough to fall into the operational events classification in the Department of Energy safety framework.[59]

To compare these fuels, a likely event of a small leak of a few gallons is used as a basis for comparison. Any of the three gaseous fuels stored at room temperature under pressure and leaking a few kg will pose the hazard of potentially igniting the gas jet at the release point with a weak ignitor. Coutts examined U.S. national fire data and calculated that there was a 0.1 average probability of a gas explosion given ignition of a flammable gas, with lower and upper bounds of 0.03 and 0.4, respectively.[68] This estimate was based mainly on natural gas indoor use in the U.S. This 0.1 probability value is useful when developing gas release scenarios. According to the data presented by Coutts, a flash fire or fireball is the most likely result of a pre-mixed gas ignition in air. Table V gives the estimated probabilities of ignition given a spill. Hydrogen may ignite itself, and the other gases would need a low energy external ignition source. Even if the gaseous fuels are stored as cryogens and a small breach occurs, the exhausting cold gas could be ignited by a reasonably strong ignitor. A burning gas jet could present significant hazards, including flame impingement on a person, radiant heating injuries, and ignition of secondary fires. A few kg of gas in a puff release to the air (e.g., relief valve lift and reseat) without combusting at the release point could be ignited early by a small energy spark and, by virtue of the small mass, produce a flash fire without any appreciable overpressure. Radiant heat from a flash fire could possibly ignite secondary fires, burning persons nearby and possibly igniting their clothing. A few gallons of gasoline released as a liquid spilled from a refueling port would seek the lowest level and would evolve flammable vapors. The vapors could be ignited by a small energy spark and the heat given off could ignite secondary fires (e.g., a person's clothing).

For this comparison of small leaks, the gaseous fuels would appear to offer the highest risk of either a burning jet or a burning cloud, and hydrogen has the highest ignition probability. For gasoline, the ignition probability in Table V is reasonably low, and the liquid will only offer a pool fire.

Gasoline has had a long history of more than 100 years of usage in the U.S.[69] and its properties are well known by fire departments. Initially, gasoline was sold in tins and bottles off the shelf in mercantile stores. Then storage tanks and pumps were used because the demand for gasoline increased and bulk liquid handling was needed to meet the demand. Over time, appropriate codes and standards were developed to provide safety in dispensing and handling gasoline fuel. Other gaseous fuels, notably CNG and LPG, have found use as vehicle fuels in the U.S. and abroad. Both fuels have had codes developed for proper handling.[17–19] It is expected that as alternate fuel usage continues, the safety standards and public appreciation of the hazards will mature. This can also be true for hydrogen fuel if usage increases. As an initial point of application, using CNG standards should provide a level of safety with use of hydrogen fuel.[45]

IV. CONCLUSIONS

This paper has presented a safety comparison of several gaseous motor fuels and the presently used liquid gasoline fuel. Because all motor vehicle fuels have a necessary requirement for flammability and high energy release when burning, no fuel can be considered safe. Regarding physical hazards, gasoline was the most benign of the four fuels discussed because gasoline is stored as a low-pressure, ambient-temperature liquid and uses a low flow rate that is easily dispensed. All four fuels have a concern for electrostatic charge production and safe dissipation of electrostatic energy. The gaseous fuels currently require, or will require, more robust engineering controls than gasoline to provide safety in refueling operations to protect against pressure and/or cryogenic hazards.

Regarding toxicity of fuels, gasoline is the highest toxicity fuel of the four because the benzene constituent of gasoline is a known carcinogen and bulk gasoline is labeled as a possible carcinogen. Gasoline intrusion into the environment is a continual source of concern. The three gaseous fuels considered here are essentially non-toxic except that they displace air and could lead to asphyxia, which is not credible in open air refueling situations. The gaseous fuels pose much less hazard to the environment than gasoline. All four fuels discussed here would pose a potential asphyxiation hazard if they leaked into an unventilated passenger compartment of an automobile or into an enclosed space, such as a garage.

Combustion is not easily judged. In situations where a few gallons of fuel are spilled, a low flammable limit presents a higher hazard. Spilling a few gallon-equivalents of gaseous fuel would allow the possibility of a jet flame ignition or a cloud ignition, while gasoline would simply evolve vapor above the pool of liquid and the vapor might be ignited. All four fuels have low mJ spark ignition energies. Qualitatively the overall risks of gaseous fuels versus gasoline should be fairly close. This research has also shown that gasoline is ubiquitous in our society and is understood by all fire departments, followed by LPG. The other gaseous fuels are not as well understood by firefighters throughout the U.S.

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